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Note

Properties Enhancement of LVLs Modified with Some Cross-Linking Agents

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Abstract——Chemically-modified laminated veneer lumbers (LVLs) were produced and their physical properties and biological resistance were evaluated. For the chemical modification, the vapor-phase formalization and the pad-dry-cure treatment of veneers with some cross-linking agents were employed prior to lamination of the treated veneers. The vapor-phase formalization was conducted for 5, 10 and 24 hours using tetraoxane as a source of formaldehyde, and the pad-dry-cure treatments with glutaraldehyde and dimethylol dihydroxy ethylene urea (DMDHEU) were made after impregnation of their 2.5, 5 and 10% aqueous solutions. Sulfur dioxide was used as a catalyst in both treatments. Laboratory tests with a brown-rot and a white-rot fungus revealed that decay was almost completely suppressed at the high levels of treatment, and fairly eliminated at the low levels of treatment. The treatment could reduce the weight loss of specimens caused by termite attack, but the effectiveness in resisting it was not as sufficient as was decay resistance. All treated LVLs were very stable to water soaking even in the 2-hour boiling on thickness swelling as well as linear expansion along tangential direction.

Keywords: chemical-modification, cross-linking agent, laminated veneer lumber, formaldehyde, glutaraldehyde, decay, termite.

1. Introduction

For efficient utilization of lesser-used wood species or small-diameter and low-grade logs, the production of reconstituted wood products such as laminated veneer lumber (LVL), particleboard and medium density fiberboard is expected to be a potential means and increases because of their enhanced physical and mechanical properties as well as the global circumstances of forest resources.

However, only the superiority of mechanical properties, and economical and ecological affairs of these products is not enough, when they are exposed to biological and weathering hazards. It is necessary to provide these products with some other high-performance particularly in enhancing the biological resistance and dimensional stability by additional treatments such as chemical modification.

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The dimensional stabilization, and the decay and termite resistance of the wood treated with some cross-linking agents have been studied; reaction of formaldehyde with wood hydroxyl-groups has been characterized in yielding high dimensional stability with low weight gain[1]. Improvement of biological resistance by formalization has been also one of the most interested matters until recently[2-4], however, vapor of formaldehyde is toxic to human body and therefore special caution should be paid in the treating process of formalization.

For the chemical processing of cotton fabrics for permanent press and wrinkle resistance, non or low-formaldehyde cross-linking agent such as glyoxal, gultaraldehyde and dimethylol dihydroxy ethylene urea (DMDHEU) have been subtituted for formaldehyde[5]. These dialdehydes and ethylene urea compounds are known to react with cellulose materials forming the cross-linking[5].

The authors have reported that the physical properties and biological resistance of MDFs are greatly improved by vapor-phase formalization[3], and the chemical treatments using a gaseous formaldehyde or non-formaldehyde cross-linking agents with SO_2-catalyst could provide a new prospective method of producing high-performance waferboards having great decay resistance and up-graded dimensional stability[6,7].

In this paper, dimensional stability and biological resistance were evaluated on pine LVLs modified with some cross-linking agents. Pine veneers were chemically-modified by vapor-phase formalization or pad-dry-cure treatment with the non-formaldehyde cross-linking agents prior to the production of LVLs.

2. Experiments

2.1 Cross-linking agents

Three cross-linking agents used for chemical modification of veneers were tetraoxane, glutaraldehyde and DMDHEU.

2.2 Wood samples

Wood specimens with the size of 5×10 (cm) were taken from 3.0 mm-thick rotary veneer of Douglas fir (*Pseudotsuga menziesii* Franco) sapwood. They were subjected to chemical modifications before pressing into LVLs.

2.3 Treatments with cross-linking agents

2.3.1 Vapor phase treatment with formaldehyde

The vapor phase treatment was conducted using technical-grade tetraoxane as a source of formaldehyde, and sulfur dioxide as a catalyst according to the method of Minato *et al.*[8]. A 3.5 liter glass-vessel containing five specimens and 3 g of tetraoxane was pre-heated in an oven at 120°C for 15 minutes, and then was kept for 5 minutes reducing the pressure by using

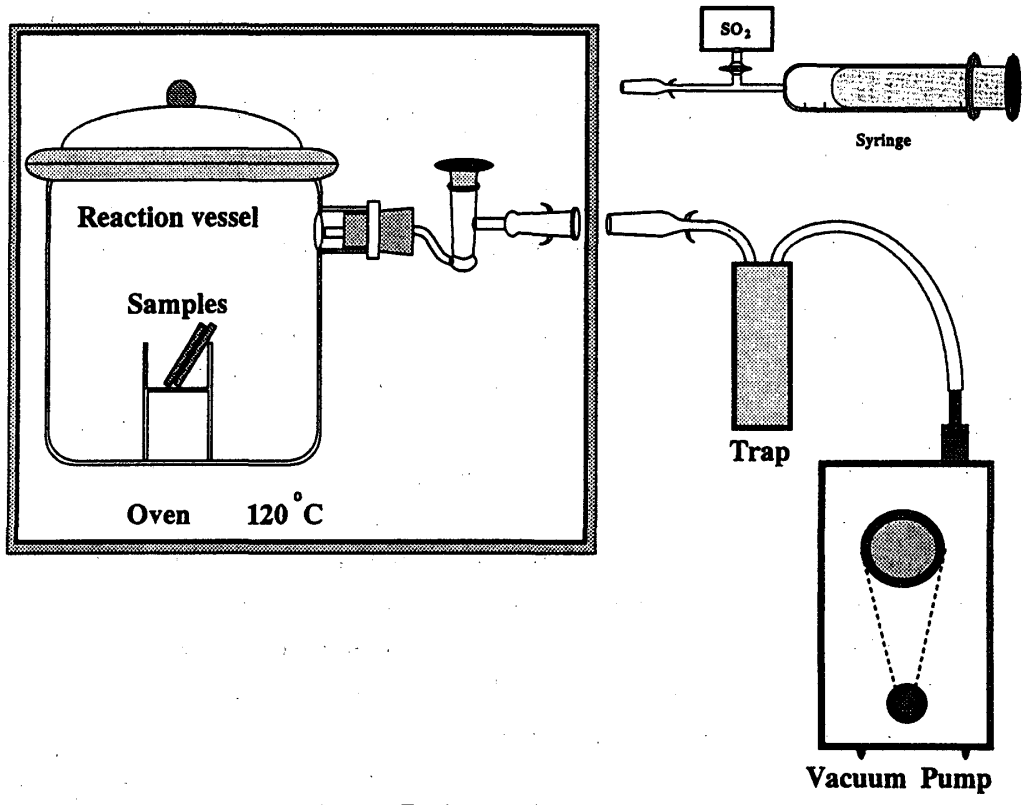

Fig. 1. Equipment for the treatment.

a vacuum pump. About 400 ml of SO_2 was introduced to the vessel by a syringe, and then whole vessel was heated at 120°C for 5, 10 and 24 hours (Fig. 1).

2.3.2 Pad-dry-cure treatments with non-formaldehyde agents

Aqueous solutions of reagent-grade glutaraldehyde and commercial-grade of DMDHEU at 2.5, 5 and 10% of concentrations were prepared, and the veneers were soaked in the solutions for more than one week until they sank to the bottom. The chemical-impregnated specimens, being air-dried in the room temperature for about one week, were put into the glass vessel previously heated to the reaction temperature of 120°C. The specimens were cured in the same apparatus as described above, however, the reaction time was fixed at 24 hours.

Treated specimens were thoroughly rinsed in running water for several days to leach out the unreacted agents from the veneers.

Weight gain (WG) in percent of each specimen was calculated from weight before and after treatment.

2.4 LVLs production

The untreated and treated veneers were pressed (5 kg/cm^2 and thickness 13 mm) into 5-ply LVLs, respectively, under room-temperature for 24 hours using resorcinol resin as a binder at about 200 g/m^2. The five treated and untreated LVLs were produced and

subjected to testing of physical properties and biological resistance.

2.5 Decay test

Conventional decay tests were made according to JWPA (Japan Wood Preserving Association) Standard No. 3-1992. Three specimens with 20 mm square of untreated and treated LVLs, respectively, were placed on a mat of the test fungus in a glass jar. A mono-culture decay test was continued for 12 weeks at 28°C using a brown-rot fungus, *Tyromyces palustris* (Berk. et. Curt.) Murr., or a white-rot fungus, *Coriolus versicolor* (L. ex. Fr.) Quél. After 12 weeks of the test period, the adherent mycelia were cleaned off, and then weight loss (WL) was calculated on the basis of an oven-dried weight of the specimen before and after test.

2.6 Termite test

The "forced-feeding test", which is described in the JWPA Standard No. 12-1992, was used to evaluate the termite resistance. One LVL specimen (20 mm square) was placed in the center of a test container of an acrylic cylinder with a barrier of hard plaster at the bottom. One hundred and fifty workers and fifteen soldiers, obtained randomly from a breeding nest of *Coptotermes formosanus* Shiraki, were introduced into each container. The test containers were assembled in a plastic box in which wet absorbent cotton was set at the bottom, and were kept at 30°C in the dark for 9 weeks. Numbers of dead termites were recorded every week to calculate termite mortality (TM). After the test exposure for 9 weeks, the specimens were removed to determine the weight loss caused by termite attack.

2.7 Water swelling test

For evaluation of the behaviors of thickness swelling (TS) on radial direction and linear expansion (LE) on tangential direction of three replications for untreated and treated LVLs, they were placed in water-bath with a controlled temperature. The specimens with 50 mm square were soaked in water at a room temperature for one day under the reduced pressure. Then they were kept in hot-water at 70°C for 2 hours, and boiling-water for 2 hours. Dimensions of the test specimens were measured immediately after taking out from water-bath on each step to evaluate the changes of TS and LE.

Changes of TS and LE for untreated and treated LVLs were also determined during the 4-cycle accelerated aging test. The specimens with 50 mm square were soaked in water for 4 days and then dried in the oven for 3 days at 60°C, and these cyclic conditions were continued for four times.

3. Results and Discussion

3.1 Weight gain

The average values of WGs for LVLs due to the treatments with the cross-linking

Table 1. WPG of veneer by treatment with cross-linking agents.

Agents	Levels	WPG (%)
(Vapor phase)	(React. time)	
Tetraoxane	5 h	0.8
Tetraoxane	10 h	1.0
Tetraoxane	24 h	1.2
(Pad-dry- cure)	(Conc.)	
Glutaraldehyde	2.5%	1.4
Glutaraldehyde	5 %	4.7
Glutaraldehyde	10 %	7.2
DMDHEU	2.5%	−0.5
DMDHEU	5 %	5.6
DMDHEU	10 %	8.6

agents are shown in Table 1. The WG was highest in DMDHEU, and followed by glutaraldehyde and formaldehyde. The values of WGs were relatively small for the formaldehyde-treated LVLs in vapor phase, and revealed no significant difference among the reaction times examined.

Those values were increasing with increases of the concentration of the solutions on both pad-dry-cure treatments, and reached about nearly 10% at the highest concentration of DMDHEU. This would mean that the dimensional stabilization due to these agents might be attributed to the bulking effect to some extent, even though the cross-linking should exist as suggested by Yasuda *et al.*[9].

Negative values of WGs in the lowest concentration of DMDHEU might be caused by that the degradation of wood components; the amount of the wood components leached away might be greater than that of the introduced chemicals at the lowest concentration of the solution, even the molecule size of DMDHEU was biggest among the agents used.

3.2 Biological resistance

The WLs of untreated and treated LVLs after 12 week exposure to the brown-rot fungus, *T. palustris*, and the white-rot fungus, *C. versicolor*, are shown in Figs. 2 and 3. The WLs of untreated LVLs after exposure to *T. palustris* and *C. versicolor* were about 40% and 29%, respectively.

The LVLs treated with vapor phase formalization for 0.8% of WG showed the relatively small WLs of 2.2 and 3.4% after exposure to *T. palustris* and *C. versicolor*, respectively. The average values of WLs decreased with increases of WGs for treated LVLs, and almost complete elimination of decay was gained after 24 hours of reaction time (1.2% of WG). However, according to our previous reports, the WLs of treated albizzia waferboards were nil even at five hours of reaction time, and 12 hours of reaction time was

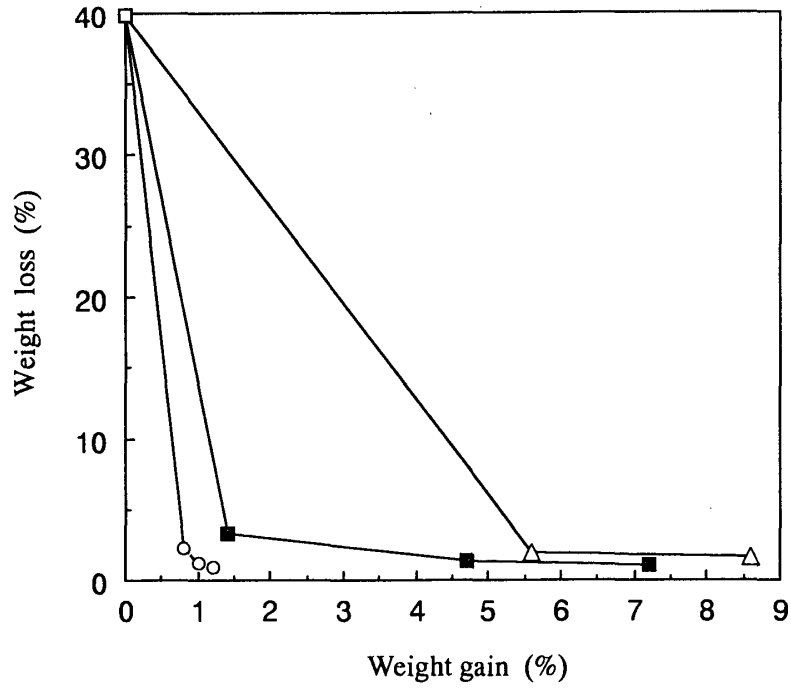

Fig. 2. The weight loss of LVLs treated with cross-linking agents after 12-week exposure to brown-rot fungi of *T. palustis*. Legend: —□— Untreated, —■— Glutaraldehyde, —○— Formaldehyde, —△— DMDHEU.

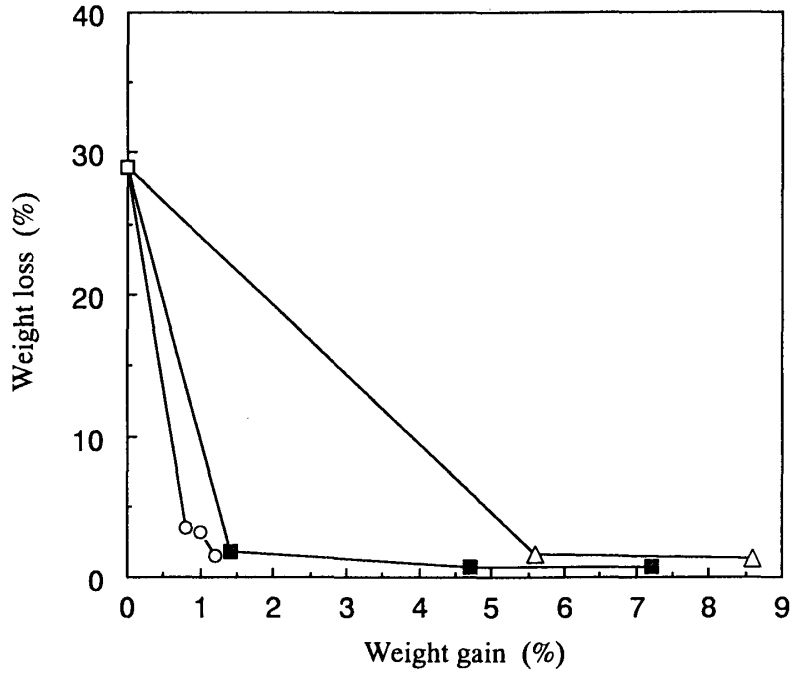

Fig. 3. The weight loss of LVLs treated with cross-linking agents after 12-week exposure to brown-rot fungi of *C. versicolor*. Legend: See Fig. 2.

required for solid-wood blocks of Japanese cedar with the small dimensions[2]. The penetration and the reactivity of the gaseous formaldehyde to the specimens affect the reaction of this cross-linking agent with wood substances.

In the pad-dry-cure treatment, the glutaraldehyde- and DMDHEU-treated LVLs also showed the relatively small WLs in all levels of the chemical concentrations. The values of WLs for glutaraldehyde-treated LVLs decreased with increasing the WGs after attacks by both decay fungi, but those of WLs for DMDHEU-treated LVLs were not significantly different among the applied WGs. The glutaraldehyde- and DMDHEU-treated LVLs needed higher WGs than the formaldehyde treatment in vapor phase to eliminate the decay attack by both fungi. This suggests that the bulking due to the impregnation of these two agents played the major role in the effect, although the cross-linking may exist to some extent.

It has been pointed out that the unreacted agents remained in wood specimens after those treatments might show some toxic effects on the wood-attacking micro-organisms. However, in our process, the treated samples were evacuated at 105°C for 6 hours for vapor-phase treatment, and rinsed in running water for pad-dry-cure treatment to eliminate the residues of the reaction chemicals. The over-growing of fungal mycelium on treated LVLs showed the non-existence of toxic effect in them, as reported previously[10,11].

In our previous report[3,4], the formaldehyde-treated wood was more effective against the white-rot fungi than the brown-rot fungi as observed in acetylated wood and another chemically-modified wood[11]. The reason was attributed to the preferential reactivity of lignin to the chemicals conducted, and to the different decay-inhibiting effects due to the cellulolytic enzyme systems between the two fungi of brown-rot and white-rot[13]. However, in these treated LVLs *C. versicolor*, a white rotter, caused the larger WLs than *T. palustris*, a brown rotter, for the vapor phase treatment, and only small differences of WLs were observed for the pad-dry-cure treatment. This suggests that brown-rot fungi were more susceptible to aldehyde treatment rather than white-rot fungi.

Incidentally, the adhesives used in the manufacture of reconstituted materials are of great importance for the fungal growth, as urea-melamine and isocyanate resins can have a promoting effect, and phenolic resins an impeding effect. It has been reported that unleached phenol-formaldehyde boards showed some toxicity to a brown-rot fungus in sand-block decay tests[13]. The presence of some soluble toxic materials in the resorcinol resin used in this experiment might inhibit or slow the attack by *T. palustris*.

The WLs of the untreated and treated LVLs after the force-feeding test by termites of *C. formosanus* are shown in Fig. 4. The average value of WLs of untreated LVLs was about 17% after termite exposure for 9 weeks, but those of treated LVLs were below 7%. The WLs did not decreased remarkably with increases of the reaction times for vapor phase treatment and the concentrations for pad-dry-cure treatment, and the effectiveness of these

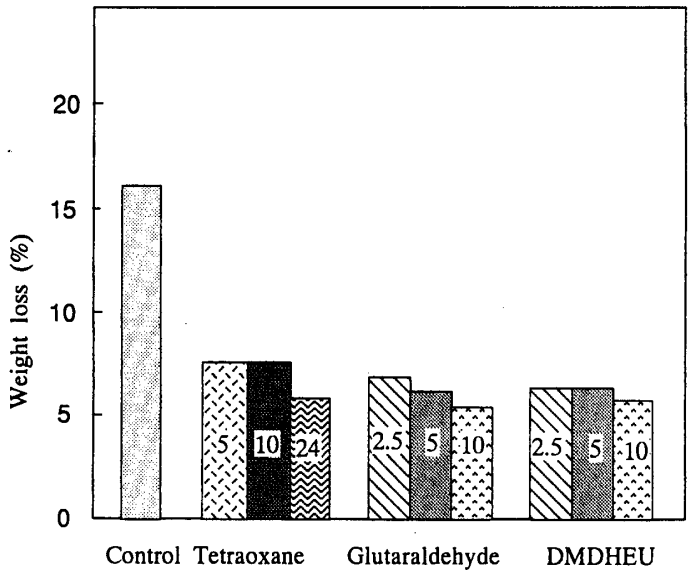

Fig. 4. The weight loss of cross-linking agents-treated LVLs after 9 week exposure to termite.
Note : Number in figure shows reaction times (hour) for tetraoxane, and concentrations of solution for glutaraldehyde and DMDHEU.

treatments in restricting the termite attack was not as sufficient as was decay resistance. Nevertheless, 100% TM was achieved by the low level of treatment within the test period of 9 weeks, whereas mortality of termites fed on untreated LVLs was below 20% at the end of the tests.

3.3 Physical properties

When LVLs are used for structural members exposed to high humidity conditions or rain fall, they should be suffered with the change of dimensions or the occurrence of cracks. Such defects have restrained LVLs from the structural use, but the high level stabilization on thickness swelling and linear expansion along tangential direction would expand the new utilization of LVLs.

Thickness swelling (radial direction) and linear expansion (tangential direction) of specimens after water soaking at room temperature and soaking in hot and boiling water are shown in Figs. 5, 6 and 7.

Values of TS of treated LVLs after soaking in water were definitely smaller than untreated LVLs, especially after soaking in boiling water. Those of untreated LVLs were about 5% after room temperature water immersion, and 6% and 7% in hot water and boiling water soaking, respectively. However, the TS values measured after each step of water swelling test decreased with increases of the reaction time for vapor phase treatment, and the solution concentrations for pad-dry-cure treatment. All treated LVLs exhibited very small TS values below 3% even after soaking in boiling water.

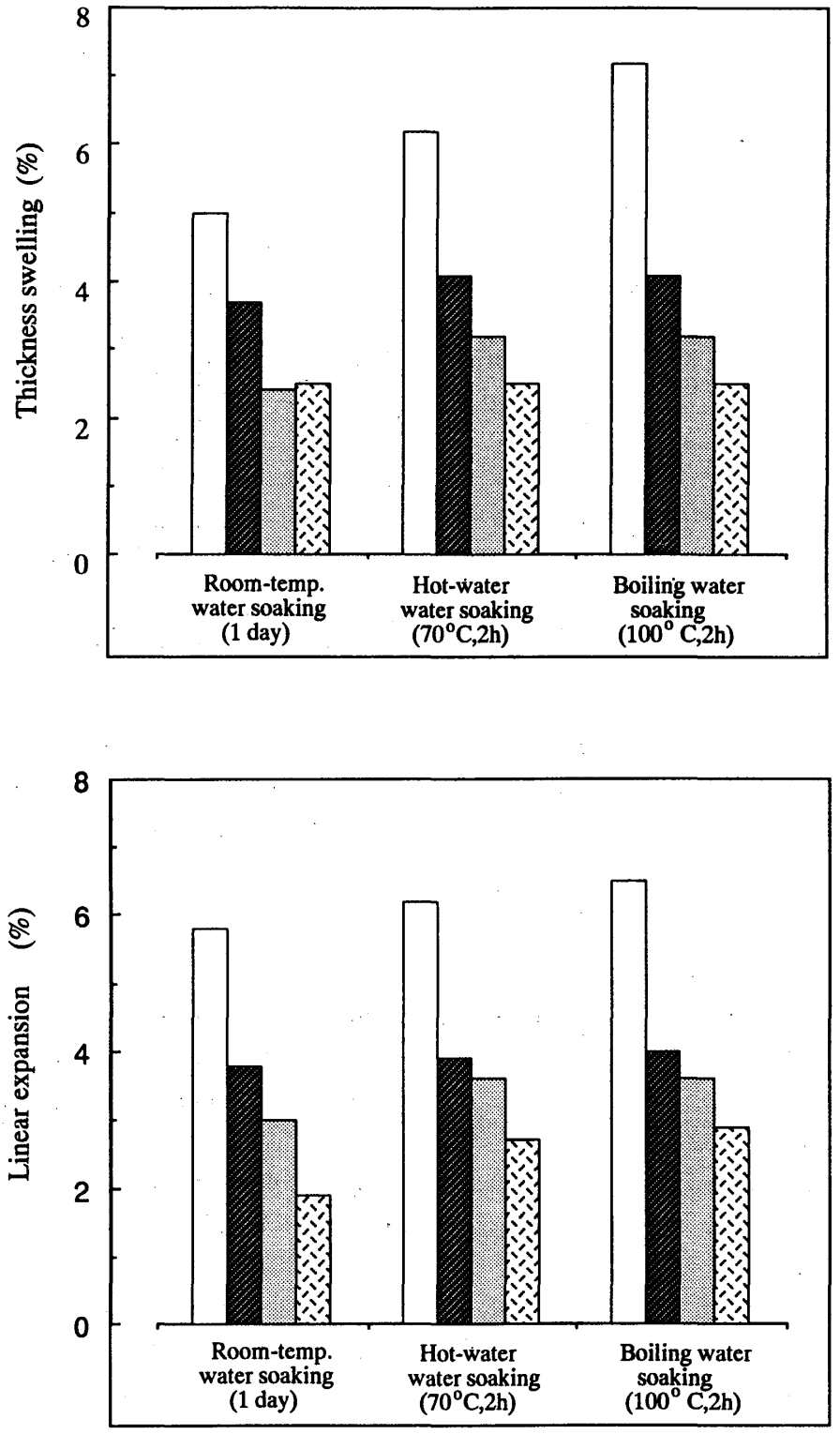

Fig. 5. Thickness swelling and linear expansion of formaldehyde-treated LVLs after water immersion.
Legend: □ Untreated, ▨ 5 h of reaction time, ▩ 10 h of reaction time and ▧ 24 h of reaction time.

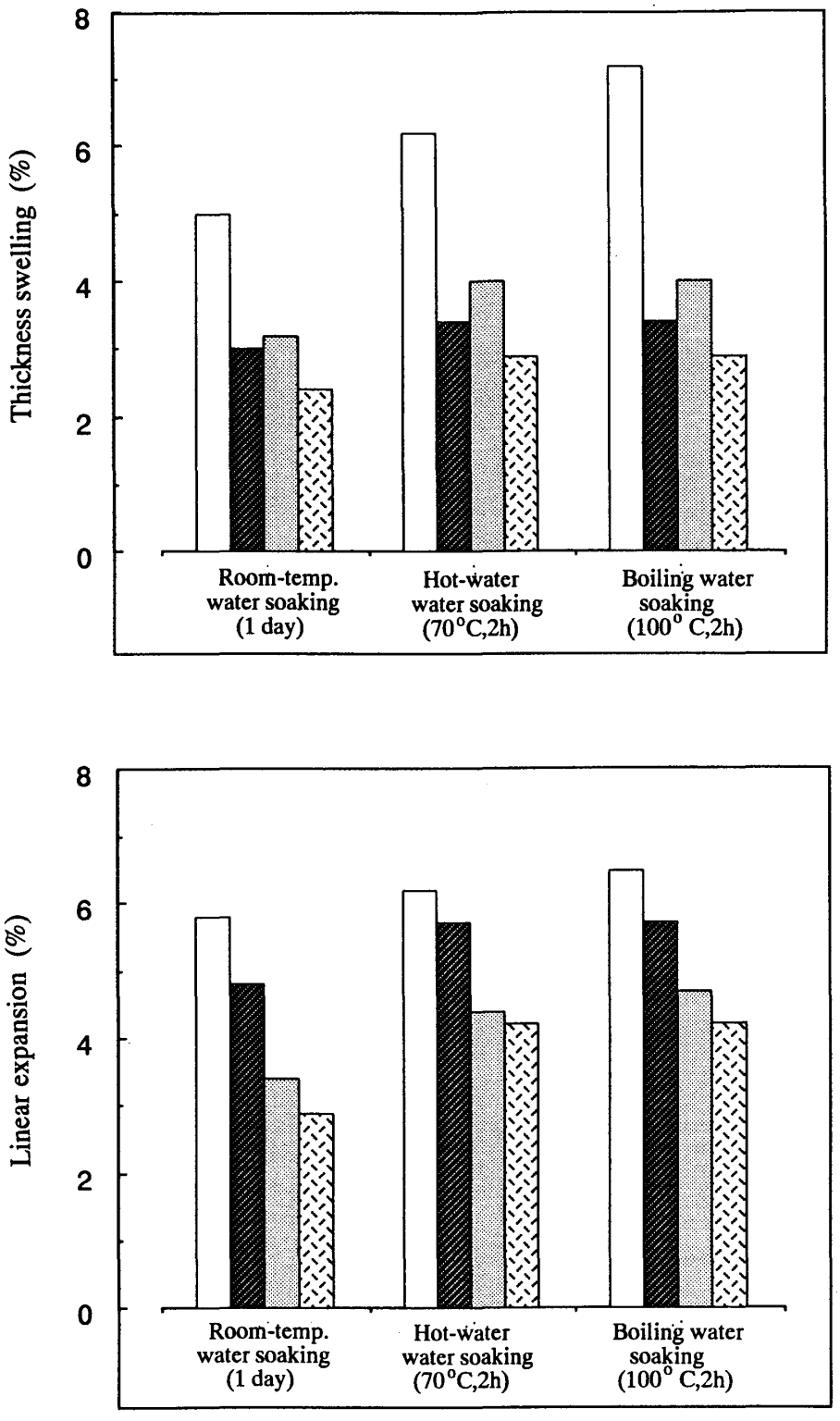

Fig. 6. Thickness swelling and linear expansion of glutaraldehyde-treated LVLs after water immersion.
Legend: □ Untreated, ▨ 2.5% of concentration, ▩ 5% of concentration and ▧ 10% of concentration.

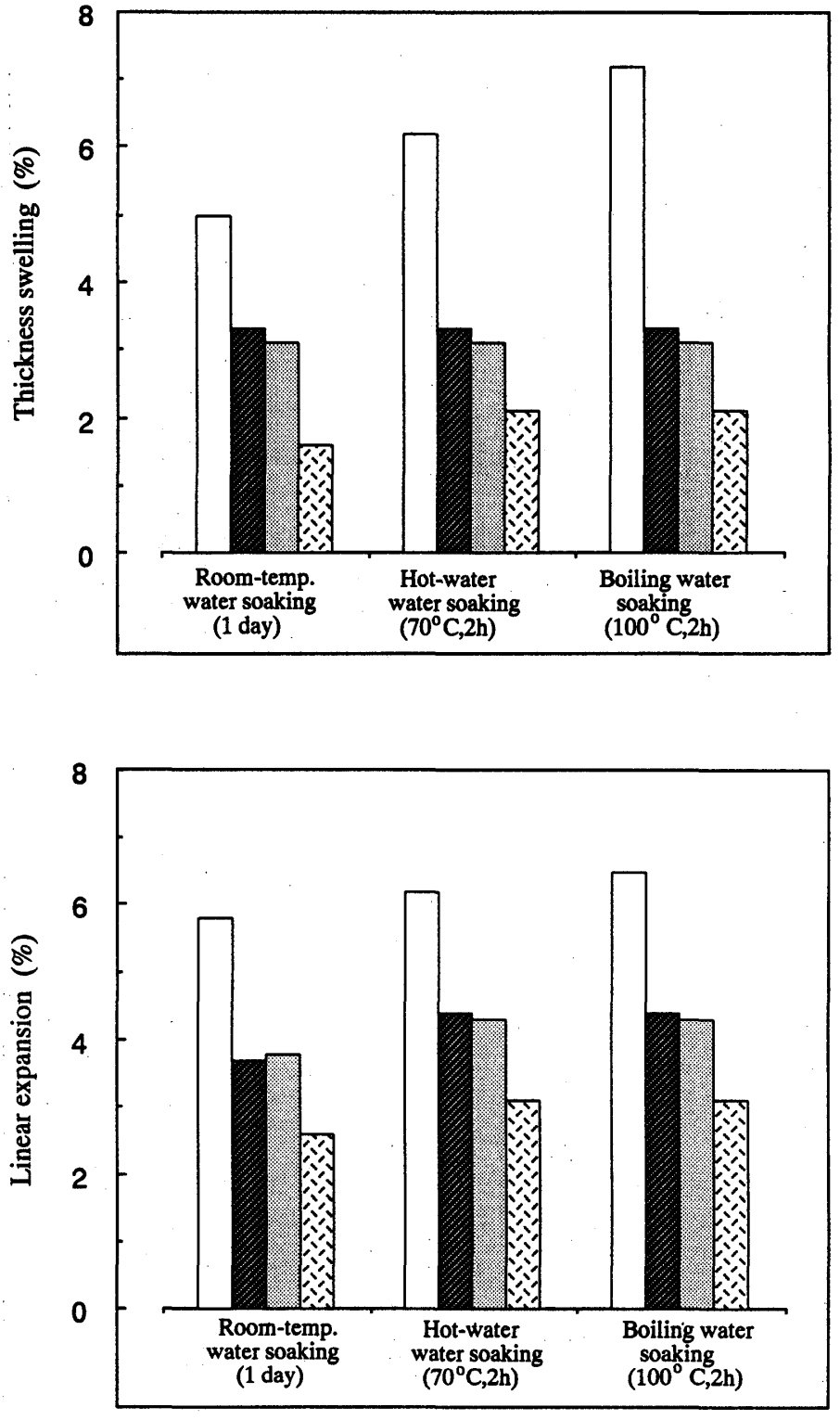

Fig. 7. Thickness swelling and linear expansion of DMDHEU-treated after water immersion.
Legend: See Fig. 6.

This should be due to the reduction of hygroscopicity of wood fibers because of the cross-linking formation in hydroxyl-groups and/or bulking in the wood cell walls. These results also indicated that the cross-linking formation by the both treatments and the bulking by pad-dry-cure treatment were stable even after soaking in boiling water for 2 hours, and that the treatments were very effective in reducing the thickness swelling and linear expansion of LVLs.

The values of LE in tangential direction decreased with increases of the reaction time for vapor phase treatment, and the solution concentrations for pad-dry-cure treatment. All treated LVLs exhibited very small LE values below 3% for formaldehyde and DMDHEU treatment, and of about 4% for glutaraldehyde treatment even after soaking in boiling water.

The changes of TS and LE of untreated and treated LVLs after 4 cycles of the soak-dry aging tests at room temperature are shown in Figs. 8 and 9. Resoaking of untreated LVLs in water caused additional irreversible stresses to be relieved and greater thickness swelling was observed than during the first soaking cycle (Fig. 8). These dimensional changes were also detected for the LVLs with low level treatments. However, treated LVLs at the highest levels of reaction time for vapor phase treatment and the solution concentration for pad-dry-cure underwent much less swelling through the soaking-drying cycles.

In the case of the linear expansion along tangential direction, additional increases of LE

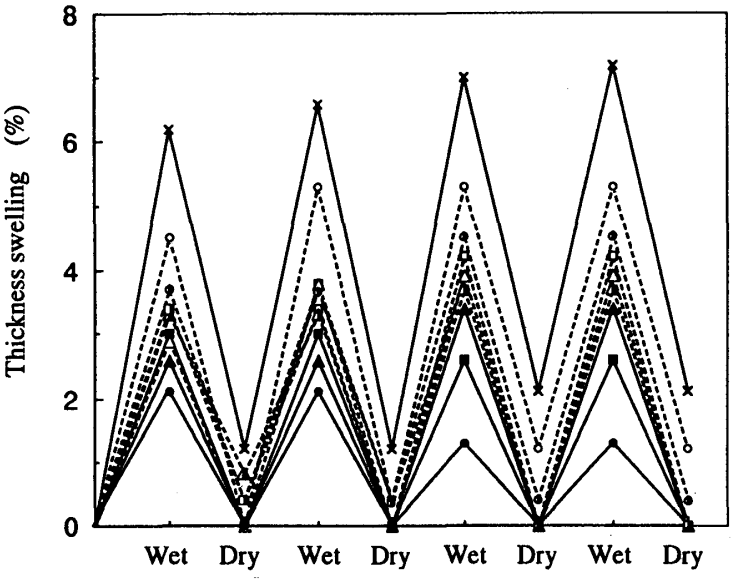

Fig. 8. Thickness swelling of untreated and treated LVLs after 4-cycle dry and wet aging test.
Legend: —×— Untreated, ---○---, ---○---, —●—; formaldehyde treatment for 5, 10 and 24 h of reactions, respectively. ---△---, ---△---, —▲—; glutaraldehyde treatment for 2.5, 5 and 10% of solutions, respectively. ---□---, ---□---, —■—; DMDHEU treatment for 2.5, 5 and 10% of reactions, respectively.

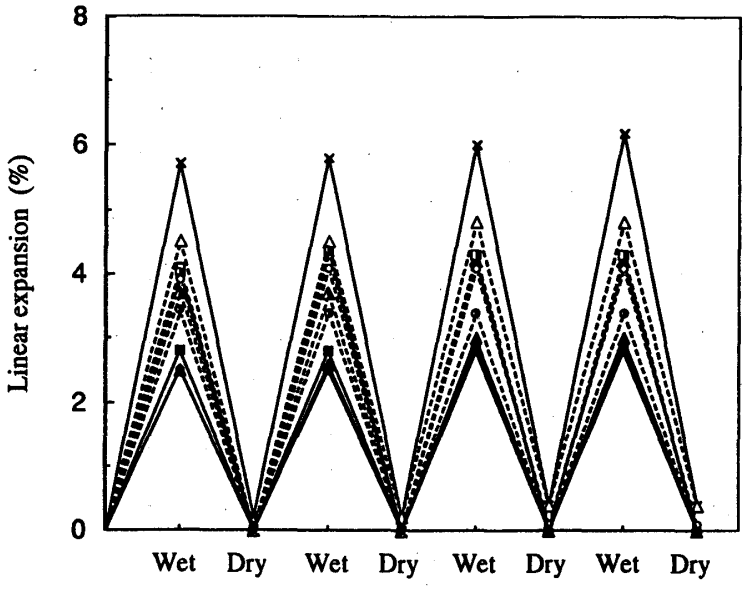

Fig. 9. Linear expansion of untreated and treated LVLs after 4-cycle dry and wet aging test.
Legend: See Fig. 8.

for untreated LVLs and its prevention for treated LVLs during soaking-drying cycles was hardly detected, but the dimensional changes were evidently suppressed by the introduction of these chemical modification (Fig. 9).

No delamination of veneers along the glue line was visually detected for untreated and treated LVLs after soaking in boiling water.

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References

1) A.J. Stamm and R.H. Baechler: *Forest Prod. J.*, **10**(1), 22–26 (1960).
2) K. Minato, S. Yusuf, Y. Imamura and M. Takahashi: *Mokuzai Gakkaishi*, **38**, 1050–1056 (1992).
3) K. Minato, S. Yusuf, Y. Imamura and M. Takahashi: *ibid*, **39**, 190–197 (1993).
4) S. Yusuf, Y. Imamura, M. Takahashi and K. Minato: *ibid*, **41**, 223–228 (1995).
5) J.G. Frick, Jr. and R.J. Harper, Jr.: *J. Appl. Polymer Sci.*, **27**, 983–988 (1982).
6) S. Yusuf, Y. Imamura, M. Takahashi and K. Minato: *Mokuzai Gakkaishi*, **41**, 163–169 (1995).
7) S. Yusuf, Y. Imamura, M. Takahashi and K. Minato: *The Int. Res. Group on Wood Preserv.*, Bali, Indonesia, Document No. IRG/WP/40018 (1994).
8) K. Minato, R. Yasuda and H. Yano: *Mokuzai Gakkaishi*, **36**, 990–996 (1990).
9) R. Yasuda, K. Minato and M. Norimoto: *Wood. Sci. and Technol.*, **28**, 209–218 (1994).
10) S. Yusuf, Y. Imamura, M. Takahashi and K. Minato: *Proc. of the Int. Symposium on the Utilization of Fast*

Growing Tress, Nanjin, China, p. 207–216 (1994).
11) W. DEWISPELAERE, J.V. RAEMDONCK and M. STEVENS: *Mat. Organismen*, **12**(3), 211–222 (1977).
12) S. YUSUF, Y. IMAMURA and M. TAKAHASHI: *Mokuzai Gakkaishi*, **35**, 633–639 (1989).
13) M. TAKAHASHI, Y. IMAMURA and M. TANAHASHI: *The Int. Res. Group on Wood Preserv.*, Finland, Document No. IRG/WP/3540 (1989).
14) Y. IMAMURA: In "Recent Research on Wood and Wood-based Materials" ed. by N. Shiraishi, M. Kajita and M. Norimoto, Current Japanese Material Research No. 11, Elsevier Applied Science, p. 75–84 (1993).